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Environmental Transport of Plutonium: Biogeochemical Processes at Femtomolar Concentrations and Nanometer Scales

A. B. Kersting, M. Zavarin

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LLNL SFA OBER–SBR FY14 Program Management and Performance Report:

Environmental Transport of Plutonium: Biogeochemical Processes at Femtomolar Concentrations and Nanometer Scales

Program Manager: Annie Kersting

Lead Scientist: Mavrik Zavarin

Current Collaborators:

LLNL: Yongqin Jiao, Robert Maxwell, Pihong Zhao, Zurong Dai[1], Scott Tumey, James Begg, Harris Mason, Ben Jacobsen, Mark Boggs, Steven Harley, Claudia Joseph, Chad Durrant

Clemson University: Brian Powell, Trevor Zimmerman, Jennifer Wong, Hilary Emerson, Nathan Conroy

UC Davis: William Casey, Adele Panasci

Cal State East Bay: Patrick Huang

University of Illinois: Yuji Arai

CIEMAT Madrid, Spain: Tiassana Missana, Ana Benedicto-Cordoba

PNNL: Andrew Felmy

Lawrence Berkeley National Laboratory: Ruth Tinnacher

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1.   PROGRAM OVERVIEW

A major scientific challenge in environmental sciences is to reliably predict and control the cycling and mobility of actinides. Plutonium (Pu) is of particular concern as over 2200 metric tons have been deposited in the subsurface worldwide. This, along with its long half-life and toxicity, represents a significant long-term environmental risk. Field measurements have documented Pu transport on the scale of kilometers. However, a reliable predictive capability for Pu migration has yet to be developed. Our predictive modeling capability is limited by scientific gaps in identification and quantification of the dominant biogeochemical processes controlling actinide transport. A mechanistic understanding of the surface structure and reactivity of coupled Pu–mineral, Pu–organic ligand, and Pu–microbe interfacial processes is needed to advance our understanding of the fate and transport of Pu in the subsurface.

In addition to Pu, we have expanded our program to include the behavior of neptunium (Np), an actinide that is also highly toxic with a long half-life (^{237}Np $t_{1/2}$ = 2.14 Ma). In FY15, we will be increasing our efforts to understand the cycling and mobility of Np and its implications for long-term transport.

This Scientific Focus Area (SFA) program is designed to test the important biogeochemical processes governing colloid-facilitated Pu transport in the field. We are evaluating the biogeochemical processes operating under low (10^{-9} – 10^{-16} mol/L), environmentally relevant, concentrations and comparing them to those operating in simple, binary-system laboratory experiments conducted at high Pu concentrations (10^{-4} –10^{-9} mol/L). At environmentally relevant concentrations, one or more of the following processes will control Pu:

  A.   binary sorption to low-site-density, high-affinity colloid surface sites (*e.g.*, surface defects),
  B.   stabilization of Pu surface complexes on mineral colloids by natural organic matter coatings,
  C.   surface precipitation of Pu polymers: experimental and natural nano-colloids,
  D.   co-precipitation with colloids as a result of mineral alteration, and
  E.   direct and indirect microbial interactions with Pu and colloids.

We are selectively examining each process separately as a function of concentration and then evaluating its potential role in Pu transport. Laboratory results are being compared to field samples taken from Pu-contaminated sites (NNSS—formally NTS, RFETS, and the Hanford Reservation). The processes listed above form the basis for 5 Program Elements, each with its own hypothesis-driven research tasks. However, each Program Element includes tasks that integrate aspects of this research plan to address our central hypothesis. Program Elements include computational chemistry studies, controlled laboratory experiments, geochemical modeling, and field sample characterization efforts that address length scales from the atomic to the field scale and timescales from picoseconds to decades.

2.   SCIENTIFIC OBJECTIVES

The objective of this science program is the identification and quantification of the biogeochemical processes that control the fate and transport of Pu at picomolar to attomolar (10^{-6} – 10^{-18} mol/L) concentrations. We are investigating the roles of mineral surface defects, ternary complexes, polymerization, co-precipitation/surface alteration, as well as direct and indirect microbial interactions on the affinity and sorption/desorption rates of Pu. With the use of unique state-of-the-art facilities at LLNL such as the accelerator mass spectrometer (AMS), a NuPlasma HR IsoProbe mass spectrometer (MC-ICPMS), the Transmission Electron Microscope (TEM), and the nano-secondary ion mass spectrometer (NanoSIMS), we are conducting laboratory experiments with Pu at environmentally relevant concentrations. A primary goal of this program is to provide the DOE with the scientific basis to support decisions for the remediation and long-term stewardship of legacy sites. An example of such support is our recent examination of ultra-low Np concentrations in groundwater at the NNSS and the implications to long-term stewardship and site closure (Zhao *et al.*, 2014 in press).

3.   PROGRAM STRUCTURE

Dr. Kersting is the program manager and point of contact for this program. She is also Director of the LLNL branch of the Glenn T. Seaborg Institute (Seaborg Institute) and reports directly to the Associate Director of the Physical & Life Sciences (PLS) Directorate, Glenn Fox. Henry Shaw is the point-of-contact for LLNL's BER Programs and is the Chief Scientist for PLS reporting directly to Glenn Fox. This SFA program is managed

through the Seaborg Institute and is aligned with the Seaborg Institute's research focus on environmental radiochemistry, nuclear forensics and super heavy element discovery.

Dr. Kersting communicates BER program needs to both the Lead Scientist, Dr. Zavarin, and Program Element leads, coordinates program execution, insures financial responsibility in spending, planning, and program direction. Bi-weekly program meetings/teleconferences with all staff members leads are used to communicate progress and ensure that the program goals are being met. Each Program Element has a lead scientist that reports to both the SFA manager (Dr. Kersting) and lead scientist (Dr. Zavarin). Dr. Kersting reports to both LLNL senior management and BER (Roland Hirsch). Dr. Zavarin ensures that Program Element efforts at LLNL and collaborating institutions are aligned with the research plan.

The majority of the experimental work (Program Elements A, C, D, and E) is led by LLNL scientists under the supervision of Dr. Zavarin in his environmental radiochemistry laboratories. The organic matter stabilization experiments in Program Element B are a coordinated effort between Clemson University and LLNL. The Program Element B lead (Brian Powell, Clemson University) and his graduate students have access to LLNL through the Laboratory's Visiting Scientist Program. Characterization and isolation of microbial populations in Pu-contaminated groundwater at the Nevada National Security Site (NNSS) (formerly Nevada Test Site (NTS)) are coordinated through external programs (*e.g.*, UGTA). Groundwater and sediment sample collection at other field sites is being coordinated through targeted collaborations (e.g. Hanford Site (A. Felmy).

In addition to the roles of Dr. Kersting and Dr. Zavarin discussed above, major team members are identified below.

Annie Kersting—Geochemist. Director of the Glenn T. Seaborg Institute at LLNL, which conducts research on environmental radiochemistry and nuclear forensics. She is also the Director of the PLS postdoctoral program (~120 postdocs) and a nuclear forensics summer student program (~15 graduate students). Her research focuses on radionuclide transport in the subsurface including field studies and laboratory experiments. Dr. Kersting is the program manager for this SFA and is the lead on Program Element C: Surface precipitation of Pu polymers and field samples. She co-supervises postdocs Mark Boggs and Claudia Joseph (FY13 new hire), and coordinates all graduate students.

Mavrik Zavarin—Lead Scientist for this SFA, the Used Fuel Disposition project, and the Underground Test Area (UGTA) NTS field sampling program at LLNL. Dr. Zavarin has over 15 years experience in radionuclide chemistry at the mineral-water interface, mineral dissolution/precipitation kinetics, colloid-facilitated transport, and radionuclide reactive transport modeling. Dr. Zavarin oversees Program Elements A-E and also co-leads Program Element A: Binary sorption to low-density high affinity surface sites. Dr. Zavarin coordinates NTS field operations with UGTA for program Element E: microbial interactions. He co-supervises postdocs Mark Boggs and Claudia Joseph. He also supervises Adele Panasci, a 2013 Lawrence scholar from the W. Casey lab at U.C. Davis and holds an adjunct position at Clemson University.

Brian Powell—Associate professor, Clemson University, radiochemist. Prof. Powell's research focuses on understanding and quantifying the rates and mechanisms of actinide interactions with natural soils and synthetic minerals. He continues to be involved with experimental and modeling studies of long-term Pu vadose zone transport at the Savannah River Site. Prof. Powell is coordinating Program Element B: Stabilization of Pu surface complexes on mineral colloids by NOM. He supervises graduate students that carry out graduate thesis work as part of this project.

Yongqin Jiao—Microbiologist. Dr. Jiao conducts research at the interface between environmental microbiology and biogeochemistry. Dr. Jiao is the lead on Program Element E: Direct and indirect microbial interactions with Pu and colloids. She is currently exploring the metabolic activities of microbes and microbial communities in natural, perturbed, or engineered environments

Pihong Zhao—Radiochemist with over 20 years experience in environmental radiochemistry, waste forms, thermodynamic data measurements for actinides and development of actinides separations. Dr. Zhao serves as lab manager for the program and has daily oversight responsibility for the safety of laboratory activities as part of this SFA.

Robert Maxwell—Chemical Sciences Division Leader and Director of LLNL's NMR facility. Dr. Maxwell is a senior chemist with expertise in the application of nuclear magnetic resonance methods to the study of the structure and dynamics of materials, polymer aging & degradation, and dissolution kinetics of silica polymorphs,

Zurong Dai—Physicist, materials scientist at LLNL. Dr. Dai has more than 20 years experience in structural characterization of natural and man-made materials by using TEM. His research focuses on crystal growth and crystallography, nano-materials synthesis and characterization, experimental measurement of electronic structure and optical properties of materials. Dr. Dai is responsible for the TEM analyses.

Ross Williams—Isotope geochemist at LLNL, Dr. Williams is the laboratory manager for the Chemical Science Division's ICP-MS Facility and chief scientist for the multi-collector NuPlasma HR IsoProbe ICPMS. Dr. Williams sets the standard for isotope ratio mass spectrometry in the DOE complex. He has more than 20 years experience in actinide radiochemistry and metrology.

Scott Tumey—Radioanalytical chemist at the LLNL Center for Accelerator Mass Spectrometry (CAMS). Dr. Tumey is a key member of the heavy-isotope group at CAMS and has played a central role in developing AMS measurement capabilities for actinides. Dr. Tumey oversees the preparation and measurement of samples by AMS, and helps design laboratory experiments that take advantage of the ultralow detection capabilities of AMS.

Harris Mason—Staff Scientist at LLNL. Dr. Mason's research focuses on applying NMR spectroscopic techniques to investigate metal sorption reactions at the mineral/water interface. Dr. Mason is the lead on Program Element D: Co-precipitation with altered colloids and oversees all NMR activities as part of the SFA.

James Begg—Formally a postdoctoral fellow and currently a staff scientist at LLNL. Dr. Begg's expertise is in environmental radiochemistry and his research focuses on actinide sorption on inorganic phases, specifically Fe-oxides and clays. He co-leads the LLNL effort on Program Element A and supervises summer and graduate student research.

Mark Boggs—Postdoctoral fellow at LLNL. Dr. Bogg's expertise is in environmental organic chemistry with a focus on radionuclide interaction with organic matter and formation of ternary complexes on mineral surfaces.

Ben Jacobsen—Staff scientist at LLNL. Dr. Jacobsen's research focuses on the application of micro-analytical tools to the analysis of sub-micrometer-sized actinide particles to determine their morphological, isotopic, and compositional characteristics using, SEM and NanoSIMS. He is using the NanoSIMS to characterize field and experimental samples.

Patrick Huang—Now at Cal Sate East Bay (formally at LLNL) Computational Physicist with expertise in investigating chemical phenomena in condensed phases and at interfaces, via the use of atomic-scale simulation techniques. Recent work includes fundamental studies on the structure and dynamics of water in carbon nanotubes, as simple models for nanoscale confinement in hydrophobic environments.

4.   PERFORMANCE MILESTONES AND METRICS

Table 4.1 shows the task plan schedule since the inception of this SFA through FY17 for each of the five Program Elements. Each Program Elements is sub-divided into Tasks. All activities are closely integrated and as such, timing of specific experiments, especially as proposed in out years, may be modified. Blue demarcations show the original planned schedule, purple represents new experiments within the original tasks, orange highlights tasks stopped and green color indicates where we are requesting additional funding. The accomplishments and metrics for each Program Element are summarized below.

Table 4.1: Program Schedule	FY2010	FY2011	FY2012	FY2013	FY2014	FY2015	FY2016	FY2017
Element A: Binary Sorption to High Affinity Sorption Sites								
Task A1: Sorption envelope & isotherm experiment								
Task A2: Flow cell sorption/desorption experiment								
Task A3: Ab-inito molecular modeling								
Task A4: Surface complexation/ion exchange model development								
Task A5: Electron sources/sinks in surface mediated Pu redox processes								
TaskA6: Integrated program element experiments								
Element B: Stabilization of Pu surface complexes on mineral colloids by NOM								
TaskB1: Determination of stability constants for Pu-NOM complexes								
Task B2: Screening for enhanced Pu mobilization by NOM								
Task B3: Chemical and physical behavior of NOM-mineral surface complexes								
Task B4: Pu sorption/desorption rates in the presence of NOM								
Task B5: Integrated program element experiments								
Element C: Characterizing intrinsic Pu colloids								
Task C1: Structural behavior of intrinsic Pu nanocolloids								
Task C2: Characterization of the Pu contaminated sediments								
Element D: Co-precipitation with Altered Colloids								
Task D1: Alteration and characterization of NTS glass								
Task D2: NMR probing reaction pathways of actinide complexes								
Task D3: integration of ab initio modeling and NMR experiments								
Element E: Direct and Indirect Microbial Interactions with Pu & Colloids								
Survey of Pu interactive microorganisms *(completed)*								
Task E1: Microbial experiments: Pu-EPS interactions								
Task E2: Investigation of mechanisms of Pu-microbe interaction								
Task E3: Integrated program element experiments: Biofilm-Pu interaction in the presence of minerals								

Legend: Stopped due to budget cut | New project | Original and continuing | Restart if funding is restored

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4.a   REVIEW OF SCIENTIFIC PROGRESS

4.a.i   Brief Review of Scientific Progress

Program Element A: Binary Sorption to High-Affinity Surface Sites
(M. Zavarin: lead; J. Begg, A. Benedicto, P. Zhao, S. Tumey, and P. Huang)

The focus of Program Element A is the study of Pu sorption in simple binary systems at Pu concentrations ranging from those observed in the field (attomolar to picomolar) to those commonly used in the lab (nanomolar to micromolar). The hypothesis guiding the effort in Program A is the following:

> *Colloid-facilitated Pu transport is fundamentally controlled by binary surface-complexation phenomena occurring on sites that have a range of sorption affinities, site-specific sorption/desorption kinetics, and redox transformation rates.*

Testing this hypothesis requires the collection of sorption data over a range of (1) solution conditions, (2) Pu concentrations, and (3) colloid minerals. The kinetics of sorption and desorption are being quantified and an understanding of the underlying mechanisms controlling sorption affinities and sorption/desorption kinetics are being identified.

Task A1: Sorption Envelope and Isotherm Experiments

In FY13 we investigated Pu sorption to a Na-homoionized clay mineral, SWy-1 montmorillonite that is a primary component of bentonite. Pu(V) sorption was found to be linear over a range of initial concentrations from 10^{-6} – 10^{-16} M. In FY14 we extended our efforts to include bentonite in order to test whether Pu sorption to montmorillonite, a pure end-member clay, is comparable to sorption on bentonite, which is more representative of repository backfill material. Pu sorption experiments were performed with bentonite clay (FEBEX) received from the National Cooperative for the Disposal of Radioactive Waste (Nagra), Switzerland. X-ray diffraction yields a bentonite composition of 92% montmorillonite, 3% plagioclase, 2% cristabolite, 2% quartz and 0.6% calcite.

Pu(IV) sorption to bentonite was broadly linear at initial Pu concentrations ranging from 10^{-7} mol/L to 10^{-16} mol/L after 120 days' equilibration (Figure A1). This result complements the linear sorption behavior observed for Pu(V) on montmorillonite over the same Pu concentration range. This linearity demonstrates that both Pu(IV) and Pu(V) adsorption to clays behaves in the same way at the higher concentrations used in
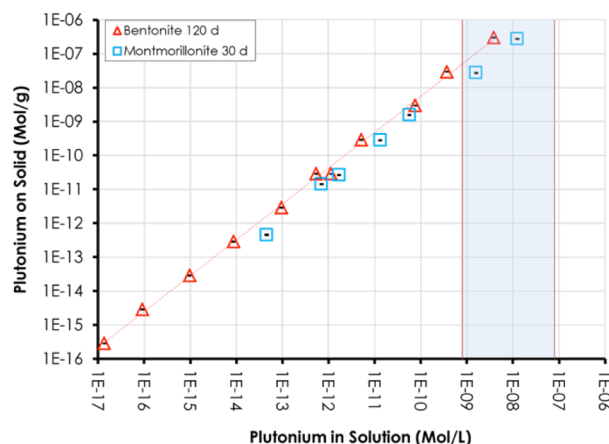

Figure A1. 120 day Pu(IV) sorption isotherm for FEBEX bentonite (triangles) and 30 day Pu(IV) sorption isotherm for Na-montmorillonite (squares) in 0.7 mM NaHCO₃, 5 mM NaCl buffer solution at pH 8. Shaded area represents expected region of Pu(IV) colloid formation.

typical laboratory experiments as it does at concentrations typically found in contaminated environments.

In addition to the work with bentonite, experiments were preformed to extend the FY13 Pu(IV) montmorillonite sorption isotherm from 10^{-11} M to 10^{-13} M. The result of demonstrate the linearity of the Pu(IV) adsorption isotherm on montmorillonite (Figure A1). Comparison of the Pu(IV) sorption isotherms for montmorillonite and bentonite reveals a remarkable similarity. These results indicate that Pu adsorption by bentonite is likely controlled by the montmorillonite component of the clay (92%) and that the other minor mineral phases do not significantly alter the Pu adsorption process. However, a slightly higher adsorption affinity of Pu(IV) for bentonite is observed compared to montmorillonite and is more marked at the two highest Pu concentrations. We suggest that this difference is in part due to the different equilibration period in the two experiments, 30 days for montmorillonite and 120 days for bentonite, indicating a minor, kinetically-limited sorption process. Further, the two highest Pu concentrations fall within the expected range for Pu(IV) colloid formation (highlighted in Figure

A1) and likely demonstrate some unique behavior of Pu(IV) at higher concentrations. This will be further investigated in FY15.

Importantly, our experimental data accumulated in the past three years as part of this SFA indicate that the affinity of Pu for mineral surfaces will not increase significantly at ultralow Pu concentrations (10^{-16} M) compared to higher concentrations routinely used in the laboratory (10^{-9} M). At greater concentrations ($>\sim 10^{-9}$ M), Pu can precipitate out as an oxide, showing nonlinear behavior. These results have broad implications to our conceptual understanding of processes controlling colloid facilitated Pu transport and, more broadly, to contaminant reactive transport. These results are reassuring in that processes identified at moderately high concentrations ($<10^{-9}$ M) can be scaled to processes at ultra-low environmental concentrations.

Task A2: Flow Cell Sorption/Desorption Experiments

In addition to experiments investigating the adsorption of Pu to mineral surfaces, we have continued to carry out work to study the *stability* of Pu adsorbed to montmorillonite. In FY14, our efforts have been focused on modeling Pu desorption from SWy-1 montmorillonite at pH 6 and pH 8 (no appreciable desorption of Pu from montmorillonite was observed at pH 4). In each experiment, Pu(IV) and montmorillonite were equilibrated for 21 days (adsorption phase) and the flow cell desorption experiment was performed for 12 days (desorption phase) after which the experiments were left to equilibrate for ~6 months (re-equilibration phase). These experiments have been used in conjunction with previously performed batch adsorption experiments to develop a mechanistic model which describes the interaction of Pu with the mineral surface. Simulations were performed *in-toto* and appropriate constraints were placed on the individual parameters so as to provide consistency between the flow cell desorption experiments, batch adsorption information and surface mediated reduction rates reported in the literature, and experimentally measured aqueous and sorbed Pu oxidation states.
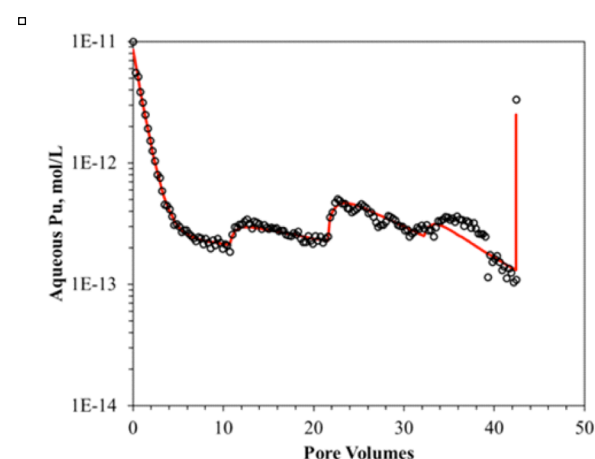

Figure A2. pH 8: Pu-montmorillonite desorption experiments performed with 0.7 mM NaHCO₃, 5 mM NaCl buffer solution at (circles) and model fit (red line).

The results of the best model fits to the data at pH 8 and pH 6 are shown in Figures A2 and A3, respectively. At pH 8, the model could effectively replicate the results of the 21 day adsorption equilibration phase (first point in Figure A2), desorption phase, and re-equilibration phase (last point in Figure A2) data. Similarly, a good fit was also produced for the pH 6 data. Importantly, at both pH values, neither non-linear nor irreversible sorption phenomena were needed to effectively replicate the data. Thus, it appears that desorption behavior is primarily controlled by first order kinetic processes that govern the adsorption, surface mediated reduction, and aging processes on the montmorillonite surface.
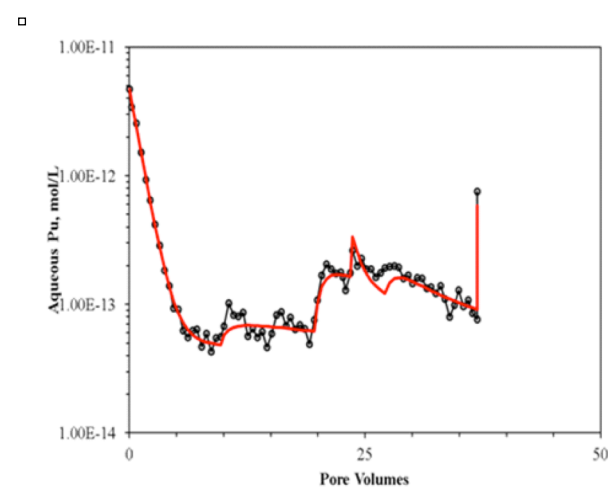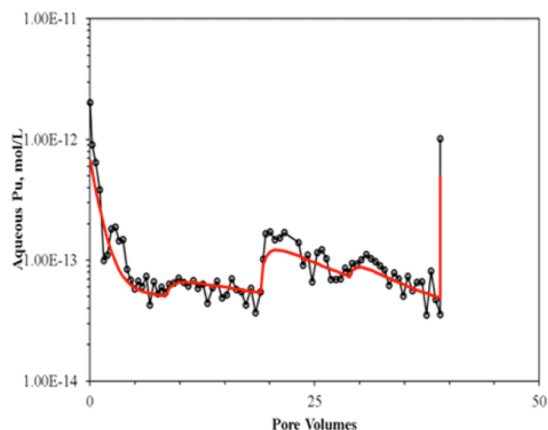

Figure A3. pH 6: Pu-montmorillonite desorption experiments performed with 0.7 mM NaHCO₃, 5 mM NaCl buffer solution at (circles) and model fit (red line).

Figure A4. pH 8: Pu-montmorillonite desorption experiments performed with 0.7 mM NaHCO$_3$, 5 mM NaCl buffer solution at (circles) and model fit (red line) following 6 months of adsorption.

To test the effect of the adsorption equilibration period, the pH 8 experiment was re-run using a montmorillonite suspension which had been allowed to equilibrate during the adsorption phase for 6 months. This pH 8 flow cellexperiment is plotted in Figure A4. Not only was the Pu solution concentration lower at the start of desorption in the 6 month equilibrated system as compared to the 21 day equilibrated system but the total amount of Pu that was desorbed from the montmorillonite was also lower. This suggests a change in the fraction of labile Pu associated with the montmorillonite as a function of adsorption time, possibly a result of slow surface-mediated Pu redox kinetics. Again, the model could effectively replicate the experimental results.

As a result of this modeling process it was possible to ascribe minimum half-lives for Pu adsorbed to montmorillonite under the given experimental conditions. At pH 8, these half-lives were 2.6 and 3.8 years, respectively for the 21-day adsorption and the 6-month adsorption experiments. At pH 6, following a 21-day adsorption period, the minimum half-life was 2.3 years. Importantly, the overall stability of Pu on montmorillonite at pH 6 is not significantly different from pH 8, suggesting that Pu stability on montmorillonite will not be dramatically affected by pH at circumneutral pH conditions. We are currently in the process of comparing our model predictions with field data to determine if our approach provides a realistic simulation of environmental Pu transport processes.

Task A3: Ab-initio Molecular Modeling

Complementary to our experimental efforts to probe the behavior of Pu on mineral surfaces, we have also been pursuing the development and application of atomic scale, ab initio models. While such an approach offers the potential to study well-defined systems at a level of detail not possible in experiments, the presence of strong Pu f-electron correlation effects and the need to explicitly include liquid water present challenges for ab initio theory. To this end, our overall plan is to (i) develop and validate models for monomeric, aqueous Pu(IV), (ii) develop and validate models for the mineral/water interface, and (iii) combine the above to study aqueous Pu(IV) sorption at the mineral/water interface. To date, we have completed (i) and (ii). At the ultra-low concentration limit of Pu(IV), the monomeric form is expected to dominate. Kno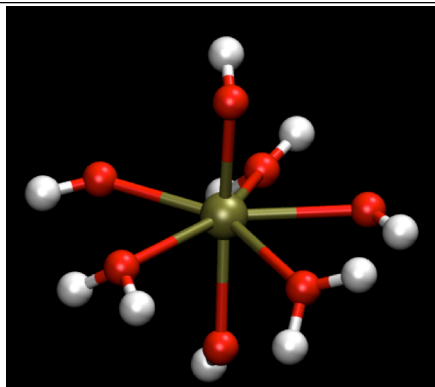wledge of Pu(IV) speciation in this regime is necessary for a mechanistic understanding of its reactivity and sorption behavior. Thus, the focus of this Task is to provide a detailed chemical characterization of monomeric Pu(IV) at a mineral/water interface, via the use of ab initio, atomic-scale simulations.

Figure A5: The hydration structure of Pu(OH)$_4$(aq) from ab initio molecular dynamics simulations, showing three strongly-bound water molecules in inner coordination sphere. The central gold atom is the Pu, red atoms represent oxygen, and white atoms indicate hydrogen. The structure is reminiscent of PuO$_2^+$(aq): there are two hydroxyl groups in the axial positions, and two hydroxyls plus three waters in the equatorial positions.

We have completed an ab initio molecular dynamics study of the interfacial water structure at the alumina(0001)/water interface, whose results were recently published in 2014 (Huang *et al*., 2014). Our findings are consistent with both the interfacial water layer structure from synchrotron X-ray reflectivity, and the interfacial vibrational spectrum from sum-frequency vibrational spectroscopy. These simulations reveal that the experimental vibrational spectrum arises from a mixture of interfacial water molecules acting as strong hydrogen bond donors to surface acceptor sites, and interfacial water molecules acting as weak hydrogen bond acceptors from surface hydroxyls.

Previously, we had also developed an electronic structure approach based on the DFT+U model (Huang *et al.* 2012) that

can treat the strong 5f-electron correlation effects in Pu(IV), but is also suitable for use in large-scale, ab initio molecular dynamics simulations. This methodology was applied to Pu(OH)$_4$(aq), which is expected to be prevalent speciation at the ultra-low concentration limit near neutral pH (Fig. A5). We find three strongly bound waters of hydration in the first coordination sphere, i.e., a Pu(OH)$_4$(H$_2$O)$_3$ complex (Fig. 5A). Interestingly, the complex is reminiscent of the PuO$_2^+$(aq) structure: there are two hydroxyls (OH$^-$) in the axial positions, while the two remaining hydroxyls and three waters in the equatorial positions.

The surprising structural similarities between Pu(OH)$_4$(aq) and PuO$_2^+$(aq) suggests a possible link with the observed ease of interconversion between Pu(IV)(aq) and Pu(V)(aq). In FY15, we will study the bonding and electronic structure of Pu(OH)$_4$(aq), which will allow us to infer the mechanisms for its redox reactivity and interaction with mineral surfaces.

Task A4: Surface Complexation/Ion Exchange Model Development

In FY14 we completed experiments designed to examine how changing the cation composition of water affects the adsorption of neptunium on clay by ion exchange. Sorption by ion exchange on permanent charge sites is dependent on the composition of the clay exchange sites. These sites are commonly occupied by Na$^+$, K$^+$, Mg^{2+} and Ca^{2+} and, as such, are strongly dependent on the aqueous conditions and electrolyte composition. However, most of the studies in the literature have so far focused solely on Np(V)-Na$^+$ ion exchange with little attention paid to the other common cations (Ca^{2+}, Mg^{2+}, K$^+$). However knowledge of all of these interactions is essential for accurate prediction of Np mobility in reactive transport models. The aim of our experiments was to isolate the ion exchange mechanism of Np(V) sorption to the permanent charge sites of montmorillonite and to estimate the selectivity coefficients of Np(V) with respect to the main ions expected to be present in typical groundwater.

Np(V) sorption was examined in pH 4.5 suspensions of homoionic montmorillonite (Na-, K-, Ca- and Mg-montmorillonite). Ion exchange on permanent charge sites was studied as a function of ionic strength (0.1, 0.01 and 0.001M) and background electrolyte (NaCl, KCl, CaCl$_2$ and MgCl$_2$. Using the experimental data, an ion exchange model was developed using the FIT4FD program, which considered all experimental data simultaneously: Np sorption data, major cation composition of the electrolyte and associated uncertainties. The model was developed to be consistent with the ion exchange selectivity coefficients between the major cations reported in the literature and led to the following recommended selectivity coefficients for Np(V) ion exchange according to the Vanselow convention: $\log\left(^{NpO_2^+}_{Na^+}K_V\right)$= -0.20, $\log\left(^{NpO_2^+}_{K^+}K_V\right)$= -0.46, $\log\left(^{NpO_2^+}_{Ca^{2+}}K_V\right)$= -0.57, $\log\left(^{NpO_2^+}_{Mg^{2+}}K_V\right)$= -0.57. Both the experimental data and the estimated selectivity coefficients in this study are consistent with the limited Np(V) ion exchange and sorption data reported in the literature. The results indicate that, as expected, low ionic strengths favour Np(V) sorption when ion exchange is the main sorption mechanism (i.e. acidic to neutral pHs) and that the divalent cations Ca^{2+} and Mg^{2+} may be important in limiting Np(V) ion exchange on montmorillonite (Benedicto *et al.,* 2014).

Task A5: Electron Sources/Sinks in Surface Mediated Pu Redox Processes

Task A5 is focused on determining the role of solution Eh and various redox-active solution components on the stabilization of Pu(IV) on mineral surfaces or reoxidation/desorption as Pu(V). In FY14 we demonstrated that environmental concentrations of H$_2$O$_2$, a naturally occurring chemical, can affect the stability of Pu(IV) adsorbed to goethite, montmorillonite and quartz across a wide range of pH values. In batch experiments where Pu(IV) was adsorbed to goethite for 21 days at pH 4, 6, and 8, the addition of 5 − 500 μM H$_2$O$_2$ resulted in significant Pu desorption. Figure A6 shows the desorption
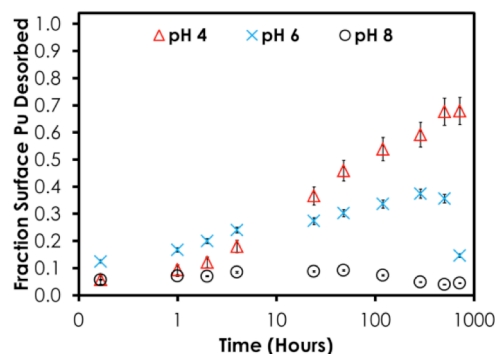

Figure A6. Pu desorption from goethite at pH 4, 6 and 8 following addition of 50 μM H$_2$O$_2$. Experiments performed with 0.7 mM NaHCO$_3$, 5 mM NaCl buffer solution and 0.1 g L^{-1} goethite.

of Pu from goethite at pH 4, 6 and 8 following addition of 50 μM H_2O_2. At pH 6 and 8 this desorption was transient with re-adsorption of the Pu to goethite occurring within the 30-day timeframe of the experiments. At pH 4, no Pu re-adsorption was observed. Oxidation state analysis of the aqueous Pu suggested that oxidation of Pu(IV) on the mineral surface to Pu(V) was responsible for the desorption process.

Experiments with both quartz and montmorillonite at 5 μM H_2O_2 desorbed far less Pu than in the goethite experiments highlighting the contribution of Fe redox couples in controlling Pu desorption at low H_2O_2 concentrations. These experiments provide the first evidence of H_2O_2 driven desorption of Pu(IV) from mineral surfaces. We suggest that this reaction pathway coupled with environmental levels of hydrogen peroxide may contribute to Pu mobility in the environment. This work was published in Begg *et al.* (2014).

Task A6: Integrated Program Elements Experiments

Integrated experiments involve the use of the flow-cell apparatus to interrogate desorption kinetics for samples prepared within other Program Elements. It also includes sample preparation (within Tasks A1 and A2) for characterization studies conducted in Program Element C. They include but are not limited to the following:

- Flow-cell desorption of Pu from ternary complex experiments conducted in Program Element B and compared to binary systems in this Program Element.
- Flow-cell desorption of natural samples contaminated with Pu characterized in Program Element D mineral alteration experiments. These desorption rates will be compared to binary desorption experiments in this Program Element.
- Samples from ternary sorption experiments (Program Element B) will also be linked to surface complexation modeling components of Program Element A (*i.e.*, Task A4).

These integration efforts began in FY12 and have continued through FY14 with the flow cell desorption of ternary complexes, and characterization of high-Pu-concentration isotherm samples by TEM. The results are reported within Program Elements B and C. The integrated experiment efforts will increase in FY15 expanding into more complex *bio*geochemical systems (*e.g.*, Program Element E) as the effort associated with binary systems (*i.e.*, Task A1) begins to ramp down in FY15.

Program Element B: Stabilization of Pu Surface Complexes on Mineral Colloids by Natural Organic Matter
(B. Powell: lead; M. Boggs, J. Wong, N. Conroy)

The focus of Program Element B is to examine the influence of natural organic matter (NOM) on Pu sorption to pure mineral phases and sediments. This program element is guided by the following hypothesis:

> *In the presence of NOM, Pu is stabilized in solution and transported through the subsurface because: 1) sorption of Pu to NOM-coated mineral colloids causes increased stability of Pu (higher affinity and slower desorption) on mineral colloids relative to the binary Pu-colloid system, and 2) formation of soluble Pu-NOM complexes* causes increased aqueous phase Pu concentrations compared to binary Pu-mineral systems.*

There are five major tasks examining this hypothesis and associated corollaries which increase in complexity from general screening experiments to detailed examination of molecular scale binding mechanisms between Pu and ligands at solid/water interfaces, and finally to the development integrated models that can predict the transport of Pu through soil in the presence of NOM. Progress in each of these tasks over the past year is described below.

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* For this discussion, "complexation" is meant to describe all chemical/physical mechanisms of TRU-NOM association and does not necessarily denote chemical bonding.

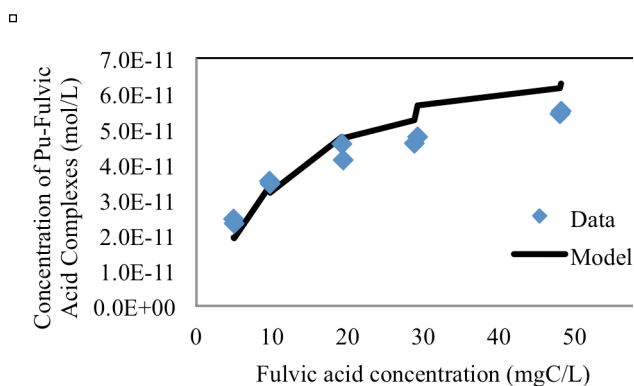## Task B1: Determination of Stability Constants for Relevant Pu-NOM Complexes

Figure B1. The concentration of Pu-FA complexes plotted against total fulvic acid concentration at pH 4, in a 10^{-10} M total Pu(IV) solution.

We have previously determined the stability constants for Pu(IV), Np(V), and Th(IV) complexation with Leonardite humic acid (Zimmerman *et al.*, 2014). In FY12 we attempted to determine the stability constants of Pu(IV)-fulvic acid complexes using PuO_2(s) solubility studies (Simpkins, 2012). While these experiments provided valuable data describing the rate of PuO_2(s) dissolution by fulvic acid, the systems did not reach equilibrium so stability constants could not be determined. In FY13 we used solvent extraction to examine Pu(IV)-fulvic acid complexation across the pH range 4-8. While modeling the data to determine the complexation constants, an experimental artifact was discovered. The extractant (PMBP) could extract into the aqueous phase at high pH, buffer the pH and compromise the data. Therefore, we determined a conditional complexation constant at pH 4 (pH where the extractant does not partition to the aqueous phase) using variable Pu concentrations. The data and model fit based upon the following reaction are shown in Figure B1.

$$Pu^{4+} + 3H_2O + HL \rightarrow Pu(OH)_3L(aq) + 4H^+ \qquad \log K = -3.18 \pm 0.03$$
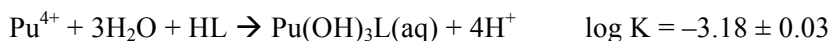
Beginning in FY15 we will use ligand competition/ultrafiltration experiments with polymerized aspartic acid (PAA) and desferrioxamine B (DFOB) to determine the stability constants of Pu-FA complexes across the pH range 3-9. These stability constants will then be used to predict Pu speciation in batch sorption and reactive transport models in Tasks B2-B5.

Task B2: Screening for Enhanced Pu Mobilization by NOM

Influence of NOM on Pu(IV) sorption to goethite

Plutonium sorption to goethite in the presence of desferrioxamine-B (DFOB), humic acid, fulvic acid, and citric acid was studied. Sorption of the NOM was also studied using radiolabeled NOM and TOC analyses. Sorption of Pu and NOM are shown in Figure B2 for experiments containing 50mgC/L NOM. Sorption models are also included in Figure B2, for the experimental system (solid line) and NOM-free (dashed line) system. Only binary sorption mechanisms were included in the given sorption models.

Previous experiments have shown that above pH 4, nearly all Pu(IV) will be sorbed to the mineral phase in a ligand-free system (Zimmerman *et al.*, 2014; Powell *et al.*, 2008). At near-neutral and high pH, the presence of NOM reduces the fraction of sorbed plutonium through the formation of soluble Pu-NOM complexes. At low pH, an increase in plutonium sorption was observed in the humic, fulvic, and citric acid experiments relative to the ligand-free system, possibly due to ternary surface complex formation.

Less than 4 % of Pu(IV) was sorbed in the presence of 50 mgC/L DFOB at any pH. At high pH values, DFOB was able to prevent plutonium hydrolysis and stabilize plutonium in the aqueous phase, indicating strong complex formation. The minimal sorption of DFOB to goethite and the formation of strong aqueous Pu-DFOB complexes appears to limit overall sorption of plutonium to goethite in the presence of DFOB.

Speciation modeling predicts that >99% of Pu(IV) will be complexed with humic acid below pH 8 in the presence of 50 mgC/L humic acid. As much as 60 % of Pu(IV) sorbed at pH 3. This decreased steadily to 26 % at pH 7. The extent of plutonium sorption follows that of humic acid sorption. However, higher fractions of Pu(IV) are often found sorbed. This is indicative of ternary complex formation or association of Pu with aggregated humic acid particles at low pH. Humic acid tends to form aggregates, particularly at low pH, which could be large enough to be centrifuged out of solution and would therefore be identified as "sorbed" based on centrifugation.

The fulvic acid system could not be modeled because Pu(IV)-fulvic acid complexation constants are only available at pH 4 (Task B1 above). Pu(IV) in the presence of fulvic acid displayed pH dependent sorption trends similar to Pu(IV) in the presence of humic acid, but with less Pu(IV) sorbed at any given pH. Likewise, less fulvic acid than humic acid was sorbed at any given pH. Generally, humic acid is thought to form stronger complexes with Pu(IV) than fulvic acid. It is therefore unexpected that higher fractions of Pu(IV) were found to be aqueous in the fulvic acid system. This could be explained by greater fractions of humic acid sorbing to goethite and humic acid aggregate formation.

Speciation modeling predicts that >99% of the Pu(IV) in the 50 mgC/L citric experiment will be complexed with citrate at pH 3, but experimental evidence shows that nearly 60% of Pu(IV) is sorbed at pH 3. This large
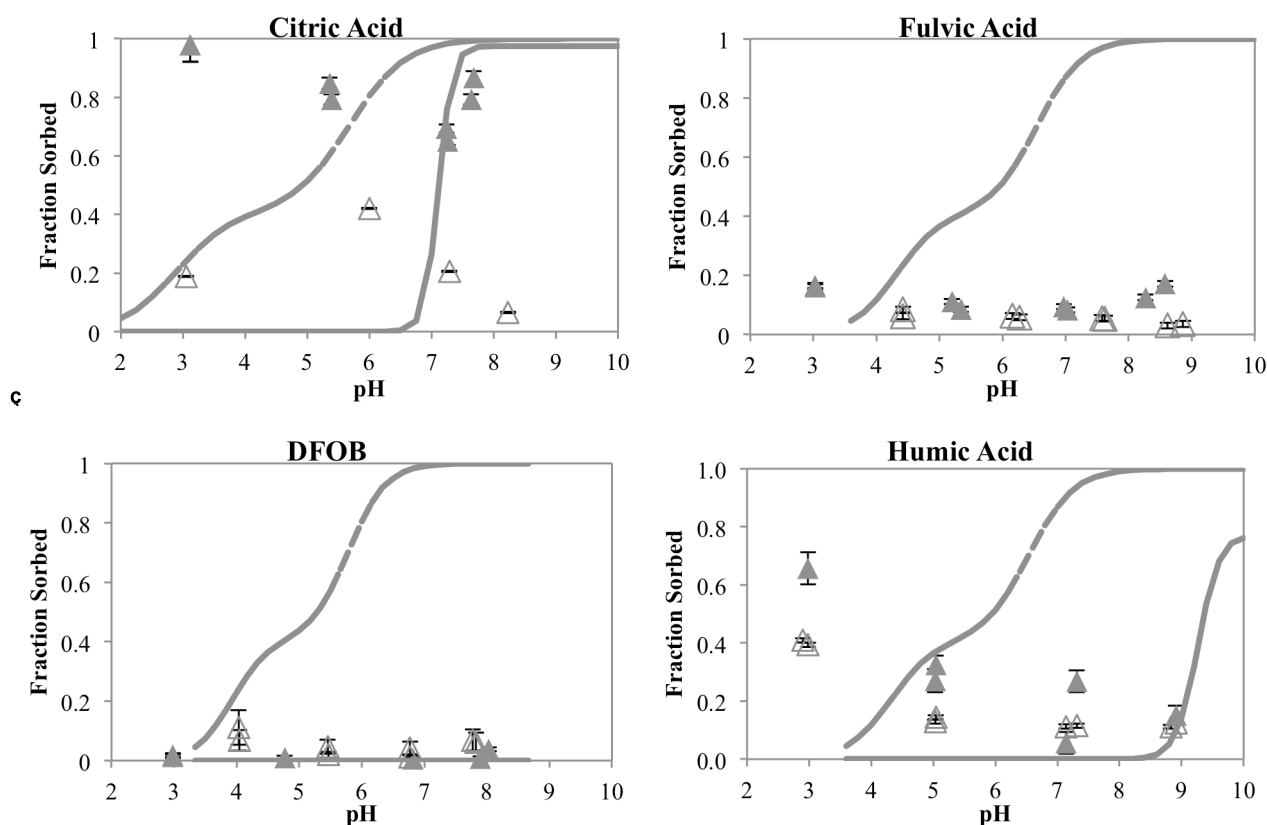

Figure B2: Influence of NOM on Pu(IV) sorption to goethite within 10^{-10} M ^{238}Pu and 50 mgC/L NOM. Closed symbols = Pu(IV) sorption, Open symbols = NOM sorption, dashed line Pu sorption model in the absence of NOM, solid line = Competitive Pu sorption model assuming only aqueous Pu-NOM complexes can form and prevent sorption (i.e. no ternary surface-Pu-NOM complexes were modeled. Note: For DFOB system the sorption model including DFOB (solid lines) predicts no sorption, thus the line falls on the x-axis. For the fulvic acid system, no competitive model is presented because Pu-fulvic acid complexation constants are unavailable across this pH range.

discrepancy indicates that 1) either the stability constants for plutonium-aqueous and plutonium-goethite speciation are incorrect or 2) that ternary surface complexes must be present. Future efforts will attempt to use radiolabeled citric acid sorption data and Pu(IV) sorption data to develop models that include ternary complexes. The spectroscopic examination of sorbed NOM complexes discussed below for Task B3 provides evidence of strong NOM association with mineral surfaces that could facilitate ternary complex formation.

Task B3: Chemical and Physical Behavior of NOM-Mineral Surface Complexes

In an effort to understand NOM sorption mechanisms, FTIR-ATR spectra of the sorbed and dried ligand-mineral systems were taken and compared to those of the pure ligand and pure mineral. From the complete spectra it was observed that the most significant region of interest was the carbonyl stretching region; generally accepted to be from 1300 cm^{-1} to 1900 cm^{-1}. This region is shown for the fulvic acid system in Figure B3.

The fulvic acid FTIR-ATR spectrum of the carbonyl region demonstrated significant changes upon sorption to goethite. The asymmetric C=O vibration observed at 1612 cm^{-1} in the "free" non-sorbed supernatant fulvic acid shifted to 1584 cm^{-1} upon sorption to goethite, and broadened somewhat. Meanwhile, the symmetric peak found at 1401 cm^{-1} in the free supernatant shifted to 1406 cm^{-1}. These shifts result in an overall decrease in the difference between the symmetric and asymmetric peak locations of 33 cm^{-1}.

Figure B3. FTIR spectra of fulvic acid sorbed to goethite (solid line) and "free" supernatant fulvic acid (dashed). All spectra were taken using FTIR-ATR single bounce diamond crystal. Vertical lines indicate peak locations of symmetric and asymmetric COO- stretches.

Previous studies of metal carboxylate complexes have found that the change in $\Delta\nu$ (where $\Delta\nu = \nu_{as} - \nu_{s}$ of the carboxylate ion; ν_{as} = asymmetric stretch and ν_{s} = symmetric stretch) between the free and sorbed carboxylate species, can be used to infer the sorption mechanism.

A difference between the symmetric and asymmetric peak locations of 33 cm^{-1} is indicative that both bidentate-mononuclear and a bridging-bidentate surface complexes could be contributors to the overall bulk sorption. The broadening of the symmetric peak is weighted more towards lower energies, which would further reduce $\Delta\nu$ and increase the change in $\Delta\nu$, and suggest that more sorbed carboxylates are sorbed by a bidentate-mononuclear complex than a bridging-bidentate.

In addition, upon sorption to the goethite surface, the C-O vibration stretch observed at 1264 cm-1 becomes very sharply defined. Further experiments suggested that the observed peak sharpening is a direct effect of fulvic acid sorption to goethite through its carboxyl functionality.
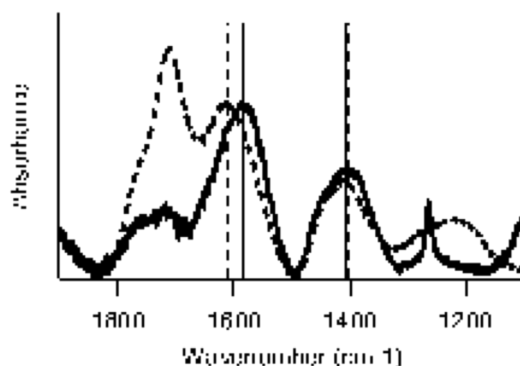
Task B4: Pu Sorption/Desorption Rates in the Presence of NOM

Flow-cell experiments were performed to estimate Pu desorption rates from goethite suspensions in the presence of citric acid and fulvic acid (Figure B4). The continuously stirred reactor chamber was 20 mL in volume and initially contained 10 mM NaCl, 0.03 g/L goethite, and 10^{-10} M total Pu(IV). All solutions were adjusted to pH 6 and contained 10 mM NaCl. To remove residual aqueous Pu, ligand-free solution was pumped until 8 chamber volumes were displaced. Then influent solution containing 0.5 mg$_C$/L (6.9 μM) citric acid or 30 mg$_C$/L fulvic acid was pumped until the termination of the experiment (3–4 days). Solutions were pumped at a rate of one chamber volume per hour. After the ligand concentration became steady, periodic stop-flow events lasting four hours were conducted to bring the system into partial equilibrium. Discrete sections of flow data were modeled with a one-dimensional reactive transport model that assumed first-order sorption kinetics. Estimated desorption rates in the presence of citric acid decrease from 6.1 × 10^{-5} to 2.1 × 10^{-5} min^{-1} over the course of the experiment. Desorption rates in the presence of fulvic acid were similar, and decrease from 7.0 × 10^{-5}
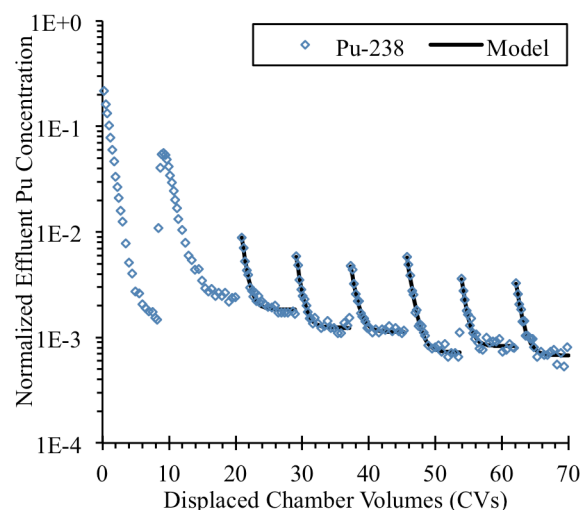

Figure B4: Effluent profile of Pu from desorption step of continuously mixed stirred flow reactor. Pu was sorbed to goethite within the reactor then desorption was initiated by adding 30 mgC/L to the influent solution. Model fits are shown in the solid lines.

to 1.4 $\times 10^{-5}$ min^{-1}. The decrease in apparent first-order rates suggests that Pu sorption kinetics on goethite suspensions may not be first-order or that overall Pu surface stability may increase with time. Future work will focus on modeling all data simultaneously and will utilize multi-site kinetic sorption models outlined in our previous work (Tinnacher *et al.,* 2011).

Task B5: Integrated Program Element Experiments

Integrated experiments between the program elements have continued through FY14..

In Program Element A and C we have learned that Pu(IV) forms remarkably strong complexes or surface precipitates on goethite surfaces. There are indications that the Pu(IV) surface complexes becomes stronger over time. Furthermore, when modeling Pu(IV) surface complexation constants it is commonly assumed the aqueous Pu is present as Pu(IV). However, based on desorption experiments in Program Element A, we learned that the dominant oxidation state in the aqueous phase is Pu(V). Thus, the modeled surface complexation constants assuming only Pu(IV) are fundamentally incorrect. We have also learned from Program Element B that 1) Pu(IV)-DFOB complexes are sufficiently strong to prevent oxidation to Pu(V) and 2) sorption of DFOB to goethite is sufficiently low to prevent formation of ternary surface-DFOB-Pu surface complexes. Therefore, batch desorption experiments in the presence of DFOB can be used to monitor the aging of Pu surface complexes and also provide data to determine the stability constants for specific Pu(IV) surface complexes without the complication of Pu(IV) oxidation to Pu(V). In these experiments, Pu was equilibrated with goethite in the absence of DFOB for various times up to 116 days. The DFOB was added to the system and Pu was desorbed for 34 and 80 days (Figure B5). Thus DFOB competes with Pu-goethite surface complexes. The data indicate that less Pu can be desorbed with increasing time and that the rate of change appears to be more rapid as the pH decreases. Modeling these data indicates that stability of the Pu-surface complex increases by approximately one order of magnitude over 116 days of aging.
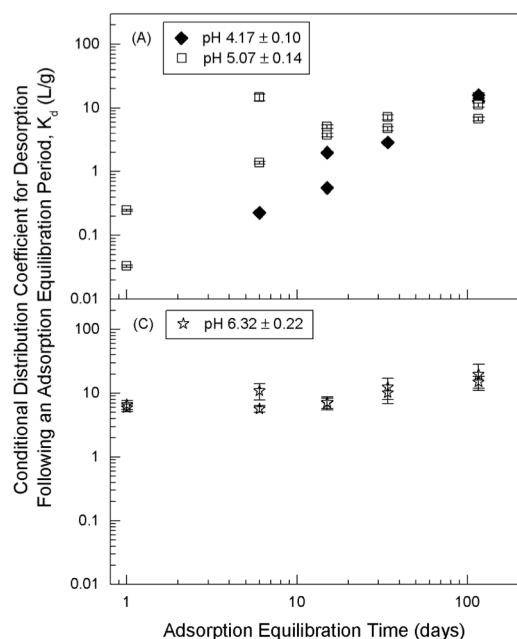

Figure B5: Conditional desorption K_d values for Pu from goethite as a function of pH and sorption equilibration time.

In FY14 we also began to examine the influence of more complicated ligands such as Extracellular Polymeric Substances (EPS) and model polymeric compounds such as polyaspartic acid (with Program Element E) on the sorption of Pu to montmorillonite and goethite. We plan to expand these studies in FY15 and also begin experiments examining soil samples from Hanford to investigate the role of organic solvents in the transport of Pu (with Program Element C).

Program Element C: Characterizing Intrinsic Pu Colloids
(A. Kersting: lead; Z. Dai, P. Zhao, M. Zavarin)

The focus of Program Element C is to determine the conditions and structure under which Pu attaches to other colloids, as either monomeric species or intrinsic colloids (Pu oxide). A secondary objective is to understand how our experimental findings compare with *natural* colloids from contaminated field sites. Program Element C is strongly integrated with Program Elements A, B, D and E. We are testing the following hypothesis:

At high Pu concentrations, the sorption behavior of Pu to mineral colloids is the result of surface precipitation of crystalline nano-colloids. The structure of the precipitate is a function of its molecular-scale relationship at the mineral-water interface. The sorption/desorption behavior of Pu colloids will be affected by its initial biogeochemical conditions ultimately influencing its mobility.

The challenge of testing this hypothesis was to carry out experiments designed to push the lower limits of detection for the TEM and NanoSIMS in an effort to interrogate Pu under the lowest concentrations and spatial scales possible (TEM: 2-5 nm and NanoSIMS: 100nm and 1ppm). To test our hypothesis, we are carrying out two projects: 1) investigating the behavior of intrinsic Pu colloids on mineral surfaces (Task C1); and 2) developing the capability of using NanoSIMS for Pu analysis on Pu-contaminated sediments from Hanford (Task C2).

Although tasks C1 and C2 are focused on understanding when Pu precipitation governs the Pu- mineral interface, our results will provide a bridge for Program Elements A, B, D, and E. Techniques employed in tasks C1 and C2 help to characterize the colloid surfaces in batch sorption/desorption experiments (Program Element A), flow-cell experiments on ternary NOM-Pu-inorganic colloid systems (Program Element B), colloids produced as a result of mineral alteration and nuclear melt glass dissolution (Program Element D), and samples prepared in the presence of microorganisms (Program Element E).

Task C1: Structural Behavior of Intrinsic Pu Nano-Colloids: Influence on Sorption/Desorption Kinetics

This research effort was restarted upon restoration of funding in FY14.

Pu transport will likely occur by association with mineral colloids or as intrinsic colloids that migrate through the environment. At high concentrations ($>10^{-9}$ M), Pu tends to form intrinsic nano-colloids. However, it is not known whether these Pu nano-colloids initially formed at high concentrations remain stable at lower (e.g., $<10^{-9}$ M) concentrations that would be expected as the intrinsic Pu colloids move down gradient from contaminated sites. We performed long-term (3 month) Pu sorption experiments at ambient and elevated temperatures in the presence of goethite (α-FeOOH) over a range of concentrations that span solubility-controlled to adsorption-controlled concentrations. We focused on the sorptive behavior of two common forms of Pu: aqueous Pu(IV) and intrinsic Pu(IV) nano-colloids at 25 and 80°C in a dilute pH 8 NaCl/NaHCO$_3$ solution. The morphology of Pu sorbed to goethite was characterized using TEM. This research was recently published (Zavarin *et al.,* 2014).

The strong affinity of aqueous Pu(IV) for the goethite surface is explained by the epitaxial growth of bcc Pu$_4$O$_7$ nano-particles on goethite (Powell *et al.,* 2011). The surface precipitation of Pu$_4$O$_7$ is affected minimally by temperature and the dispersed 3-5 nm Pu$_4$O$_7$ nano-particles appear to be stable over the timescale of months at both 25 and 80°C (Fig. C1). There is no indication that the Pu$_4$O$_7$ alters to PuO$_2$ over time. Intrinsic Pu colloids are composed of PuO$_2$ nano-particles in the 3-5 nm size range. When intrinsic Pu colloids are reacted with goethite over 103 days, TEM observations suggest that the Pu colloids have a weaker interaction with the goethite surface than adsorbed and surface precipitated aqueous Pu(IV). There is no indication that the PuO$_2$ nano-particles alter to Pu$_4$O$_7$ on the goethite surface over time. Thus it appears that the interaction of Pu with goethite is dependent on the initial state of Pu (i.e. aqueous versus colloidal) in solution. Furthermore, it is apparent that the structural distortion of Pu(IV) surface precipitates on goethite is stable on a timescale of months and unaffected by temperature.
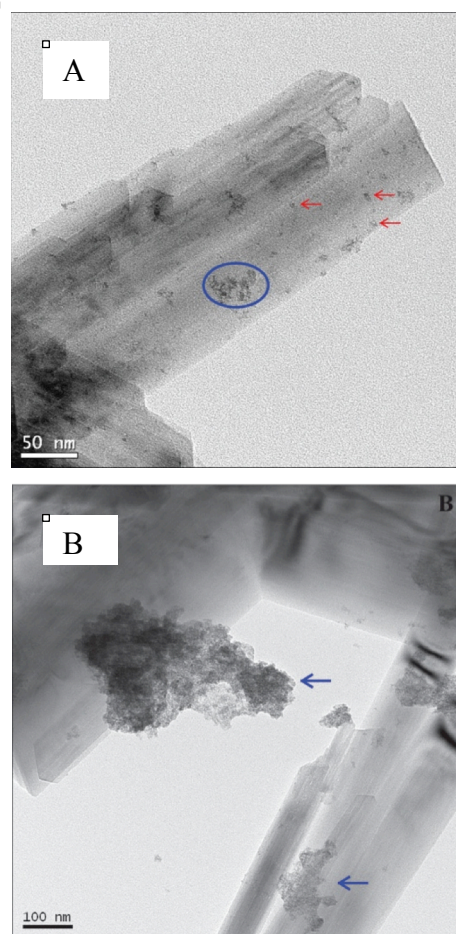
Figure C1. Both PuO$_2$ nano-particle aggregates (blue) and dispersed Pu$_4$O$_7$ nano-particles (red) on the goethite surface are observed when Pu(IV) is introduced in an aqueous form (25 and 80C) (A). However, only PuO$_2$ nano-particle aggregates (blue arrows) are observed when Pu(IV) is introduced as intrinsic colloids (B). The aggregates are located both on and off the goethite surface, indicating a weak association between PuO$_2$ and goethite.

Future research is designed to focus on the factors controlling the structural distortion of the Pu-oxide observed on goethite. Will Pu-oxide show similar epitaxial growth with minerals that share similar structure, and/or surface reactivities? How does this influence desorption behavior? We will investigate the structure of intrinsic Pu colloids sorbed to isostructural minerals such as diaspore (AlOOH) as well as other Fe-oxides with strong surface reactivity (*e.g.,* magnetite). We will also take advantage of LLNL's TEM, electron energy loss (EELs) capability to measure potential changes in Pu oxidation state.

Program Element D: Co-precipitation with Altered Colloids
(Zavarin M.: lead; R. Maxwell, H. Mason, S. Harley, A. Panasci, J. Begg, Claudia Joseph)
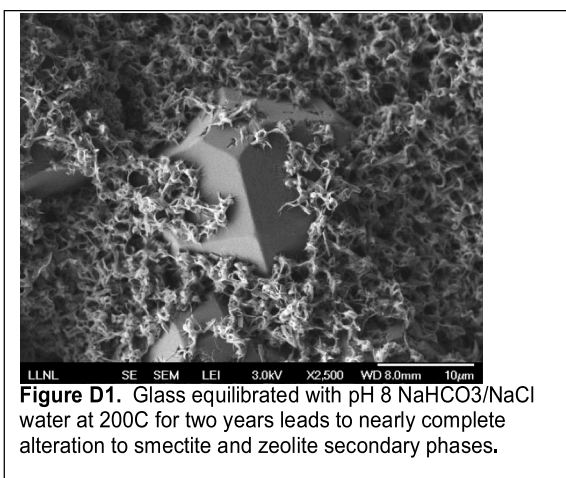
Hypothesis: Colloid formation during primary rock alteration and secondary mineral precipitation can structurally isolate Pu in colloids at environmental concentrations.

To test the hypothesis in Program Element D, we initiated two experimental tasks. The first was a series of long-term (2-year) alteration experiments on nuclear melt glass from the NTS (Task D1). Experiments will be further analyzed this year. The second task was to determine the structure of Pu in association with colloidal silicates at environmental concentrations as a function of surface loading using NMR (Task D2).

A third effort expected to start in FY15 (Task D3) will be to combine our actinide NMR studies of Pu structure on inorganic and organic surfaces with results from molecular-scale simulation of Pu at the silicate-water interface (Program Element A). The objective of this study is to capture the transition from structural incorporation of Pu in the silicates at low concentrations (monomeric) to PuO_2 precipitation at higher concentrations. All three tasks are focused on testing the hypothesis that colloid formation during primary rock alteration and secondary mineral precipitation can structurally isolate Pu in colloids at environmental concentrations.

Task D1: Alteration and Characterization of NTS Glass

Nuclear melt glass from the NNSS was hydrothermally altered at 25, 80, 120, and 200°C for over two years and sampled at regular intervals. Gram quantities of Pu-containing glass plus fluid were placed in large volume (600 mL) titanium Parr bomb vessels. Experiments were designed to produce significant quantities of secondary alteration phases for use in follow-on desorption and Pu stability experiments. Samples were collected at 1.3, 1.8, and 2.7 yrs. The experiments are now complete.

Figure D1. Glass equilibrated with pH 8 NaHCO3/NaCl water at 200C for two years leads to nearly complete alteration to smectite and zeolite secondary phases**.**

The colloidal material produced from the original melt glass consists of secondary clay and zeolite colloids (Fig. D1). Colloid concentrations and Pu concentration are temperature- and time-dependent (Table D1). However, Pu activities in solution are less than 1 nCi/L in all cases. The result provides an upper limit for Pu concentrations at NNSS. Pu desorption experiments were recently initiated using EDTA extraction to test whether Pu associated with the colloidal material will desorb. Preliminary results indicate that Pu desorption of the melt glass is much less reversible than simple surface desorption processes, which may help to explain the kilometer-scale colloid-facilitated Pu transport observed in the field.

Table D1. Summary of Pu concentrations and colloid loads in glass alteration experiments.

days	colloid load			Pu concentration			% colloidal*		
	457	644	994	457	644	994	457	644	994
		g/L			pCi/L			percent	
25	0.000	0.002	0.000	0.7	1.6	0.4	79	88	71
80	0.011	0.013	0.003	44.2	54.4	58.2	94	94	21
140	0.239	0.259	0.073	342.5	373.2	304.8	79	90	70
200	0.070	0.150	0.062	313.7	800.1	125.2	90	68	45

* >20 nm particle size

Task D2: NMR Probing Reaction Pathways of Actinide Complexes

The goal of this task is to investigate the fundamental pathways of plutonium complexation both with solution species and with solid surfaces using NMR spectroscopic methods. This task addresses the challenge of developing characterization techniques that can access information about these processes at relevant environmental concentrations. Three major achievements highlight the advances we have made in FY14.

Investigation of Np ligand exchange reactions

As we work towards the goal of understanding solution exchange kinetics of Pu, we have begun by pursuing model actinide/ligand systems. In this case we are examining ligand exchange reactions between various oxidation states of Np and water, hydroxyl, and carbonate ligands. The rate of ligand exchange for aqueous Np complexes can be experimentally determined using isotopically labeled ligands and NMR spectroscopy. Np(V) is the most stable oxidation state and exists as the "yl" ion with two axial doubly-bonded oxygens, NpO_2^+. Due to the paramagnetic nature of Np(V), attempts to determine exchange rates between equatorially bound waters and those in the bulk solution were made using ^{17}O-NMR. The chemical shift and peak width of the bulk water

Figure D2. ^{13}C NMR of 7.2 mM $[NpO_2(CO_3)_3]^{4-}$ at pH 10.1. Selectively exciting the free carbonate peak to be negative. With longer mixing time, the bound carbonate magnetization decreases as a result of magnetization transfer between the two sites.

signal for the sample containing the paramagnetic species has been found to be different from the reference, and experiments at various temperatures are currently underway to determine the rate of water exchange.
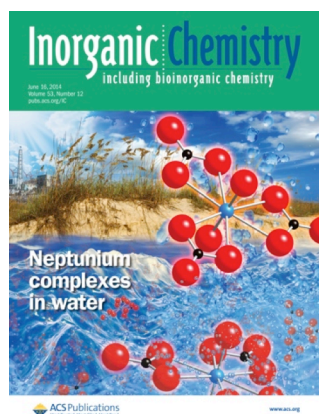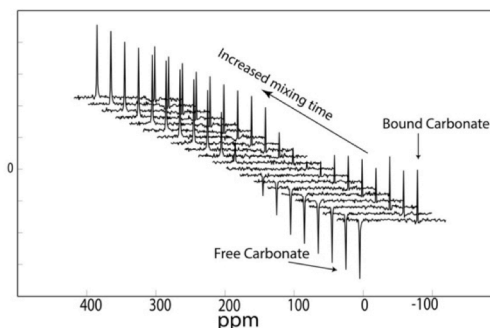
In the presence of carbonate, Np(VI) has been found to be more soluble than Np(V). Using NpO_2^{2+}, the rate law of carbonate exchange can be determined using ^{13}C-NMR. Np-carbonate NMR experiments have been modeled after the work done on U(IV) carbonato complexes (Banyai *et al.*, 1995), and the carbonate exchange was experimentally determined to be 40.6 s^{-1} for the triscarbonato complex at a pH higher than nine, $[NpO_2(CO_3)_3]^{4-}$ using a saturation transfer technique that shows the transfer of magnetization between the ^{13}C signal of the free carbonate and the carbonate bound to the neptunium (Fig. D2). Above pH nine, there was no pH dependence but as pH decreased, a pH dependent pathway was observed, which is similar to what was determined for the uranyl and plutonyl triscarbonato complexes. This work was recently published in *Inorganic Chemistry* (Fig. D3)

Figure D3. Inorganic Chemistry cover for $[NpO_2(CO_3)_3]^{4-}$ carbonate exchange rate work.

(Panashi *et al.* 2014). Further studies in FY15 will focus on measuring carbonate exchange kinetics as a function of pressure to determine the nature of the activation complexes.

This study has shown that robust structural information about Pu-NOM complexes can be acquired with advanced NMR spectroscopic methods. The information provided is critical to understanding how Pu interacts with NOM in the environment and how it may be transported. Ongoing work has been focused on utilizing the above solution state and additional solid state NMR methods to characterize the interactions between Pu and bacterial extra-polymeric substances (EPS).

Eu sorption on silica at low surface concentrations

A third project undertaken in FY14 highlights the continued use of the surface selective solid-state NMR techniques to investigate the surface sorption of paramagnetic cations towards the goal of investigating Pu/surface complexes. Previously, we have developed a method that combines surface selective $^{29}Si\{^1H\}$ CP/MAS NMR measurements with statistical analysis to elucidate the sorption of divalent paramagnetic metals, Ni(II) and Cu(II), to the surface of the amorphous silica surface at high pH (Mason *et al.*, 2012). The focus has shifted to a lower pH of 5, and to the sorption of trivalent lanthanide species. These conditions approach those examined in binary Pu(IV/V) sorption/desorption experiments investigated as part of Program Element A.

These conditions vary significantly from our previous study at high pH because of the environment present on the silica surface. At pH 8 and 9, the silica surface is dominated by deproated silanol sites ($>SiO^-$) that favor the sorption of positively charged metals. At pH 5 the surface is dominated by protonated silanol sites ($>SiOH^0$), that lead to much lower metal sorption. Supernatant concentrations monitored by ICP-MS indicated that no measureable sorption had occurred, consistent with the low capacity of the surface. However, despite the very low surface coverage, we still observed systematic changes in both the spectral, and concentration profiles of the CP/MAS kinetics (Fig. D4). These results suggest that the method can access information about the sorption of metals to these surfaces even at very low surface loadings. Additionally, ^1H spin diffusion measurements were used to produce estimates of the effective radii of the sorbing lanthanide complex. Comparing the results at differing concentrations, we observe no differences in the spin diffusion profile, and consequently predict

Figure D4. $^{29}Si\{^1H\}$ CP/MAS Kinetics for a pH 5 control sample, and three samples made with different Eu(III) loadings.

that at all concentrations the lanthanide species are evenly distributed, most likely as monomers on the silica surface. Current experiments are focused on removing the small amounts of lanthanides that are sorbed to the surface in order to determine the metal surface coverage with ICP-MS and develop models for the sorption process. Future experiments will focus on applying the above methods to Pu/mineral interactions. A proposal requesting NMR time at the EMSL Radiochemistry Annex has been submitted that will allow us to perform MAS experiments on Pu-containing samples. Of particular importance will be the investigation of polymer and surface precipitate formation which can affect the stability of Pu on mineral surfaces and, as a consequence, the effectiveness of colloid-facilitated transport.
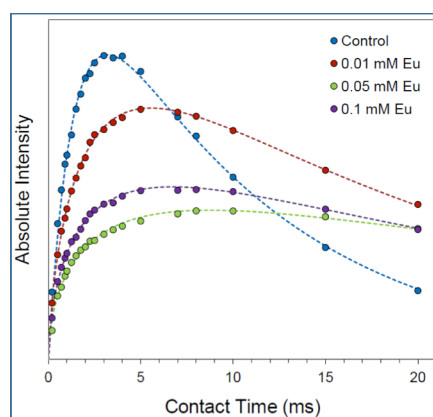
Task D3: Integration of Ab initio Modeling and NMR Investigations: Spanning Pu Behavior over 10 Orders of Magnitude Solution Concentration

Our goal in this task is to integrate results obtained from *ab initio* modeling of Pu clusters on surfaces in the presence of water at extremely low concentrations with NMR investigations of actinide-surface reactions at higher concentrations. The surface structures and reaction mechanisms of Pu species predicted by *ab-initio* modeling will be checked against the results obtained from NMR. Similarly, these predictions will be used to better constrain the pertinent experimental conditions where NMR measurements will be performed. The interplay of these two methods, both sensitive to local bonding environments, will allow for more accurate determination of reaction rates and mechanisms of Pu sorption at very low, environmentally relevant concentrations where direct EXAFS measurements are not possible. The start date for Task D3 is FY15 or FY16 depending on funding.

Program Element E: Direct and Indirect Microbial Interactions with Pu and Colloids
(Y. Jiao, Lead; M. Boggs)

Microorganisms are associated with a variety of radioactive materials at DOE sites (Barnhart *et al.*, 1980; Francis *et al.*, 1980; Fredrickson *et al.*, 2004) and it is becoming well-known that Pu speciation and solubility are affected by microorganisms (Gillow *et al.*, 2000; Neu *et al.*, 2005; Panak and Nitsche, 2001). This Program Element tests the hypothesis that:

> *Environmental microorganisms can impact the mobility of Pu by direct and indirect mechanisms at environmentally relevant concentrations.*

Most Pu microbiology to date has been performed on a handful of laboratory strains (Macaskie and Basnakova, 1998; John, 2001; Rusin *et al.*, 1994; Francis, 2007; Panak and Nitsche, 2001) and at relatively high Pu concentrations (micromolar to millimolar). The general lack of knowledge concerning the diversity, biodensity, exopolymer production potential, and direct Pu-reduction capacity of microorganisms at Pu-contaminated DOE sites is a knowledge gap that needs to be filled in order to assure that DOE's long-term stewardship goals are met.

In FY13, we began investigating the effect on Pu mobility by an environmentally relevant bacterium, *Pseudomonas sp*. strain EPS-1, isolated from the NNSS (formerly NTS) groundwater. Using ESP-1 as a model organism, our goals are to map the Pu absorption and precipitation processes, and examine the speciation and stability of Pu on the cell surface under relevant environmental conditions. We focused on characterizing cell surface structural responses and investigating the function of catalytic biomolecules that facilitate Pu precipitation at Pu concentrations relevant to the DOE sites.

To gain insight into the EPS mediated redox mechanisms controlling Pu adsorption onto cell surfaces, in FY14 we have expanded this study by examining Pu interaction with purified EPS and the EPS-bound to the cell surface. Our hypothesis is that Pu precipitation on the cell surface is catalyzed by EPS, and corresponding Pu redox chemistry occurs upon binding to the cell surface. Besides investigating the sorption and redox behavior of Pu, we used high-resolution transmission electron microscopy (TEM) to examine the morphological and structural changes at the Pu-cell surface interface. We also began using NMR to character the functional groups within the EPS that are responsible for Pu complexation and reduction.

Task E1: Microbial Experiments: Pu-EPS Interactions

The overall objective of this task is to determine how Pu interacts with extracellular polymeric substances (EPS)
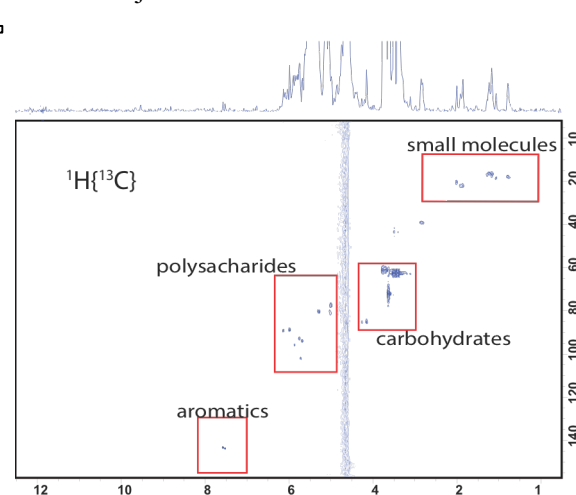

Figure E1. $^1H^2$ Heteronuclear Single Quantum Correlation (HSQC) of ^{13}C enriched EPS in D_2O

produced by the *Pseudomonas sp*. In FY14, we focused on the role of cell-bound EPS produced by *Pseudomonas sp.* strain EPS-1, a bacterium isolated from the NNSS site. EPS are biopolymers resulting from active bacterial secretion, shedding of cell surface material, cell lysis materials and from adsorption of organics from the environment. EPS is a major organizational element and provides an overall protective structural stability to the microbial community. We have focused on the cell-bound EPS because as the outermost layer of the cell surface, the bound-EPS is likely to play a major role in surface chemistry of the bacteria, and therefore affect Pu redox chemistry and its sorption.

To characterize the composition of the bound-EPS produced by *Pseudomonas sp*. strain EPS-1, we performed NMR analysis on the ^{13}C labeled EPS. The labeled EPS was obtained by growing strain EPS-1 in minimal media containing $^{13}C_6$ glucose as the sole carbon source. Comparing to non-labeled samples, enriching EPS with ^{13}C facilitates better separation and identification of functional components of the EPS and decreases the time needed to obtain a spectra by ~ 50 percent. We found the bound-EPS (separated from *Pseudomonas sp*)

consists of a complex mixture of carbohydrates, polysaccharides and aromatic compounds, which are likely the breakdown products of membrane lipids (Fig. E1).
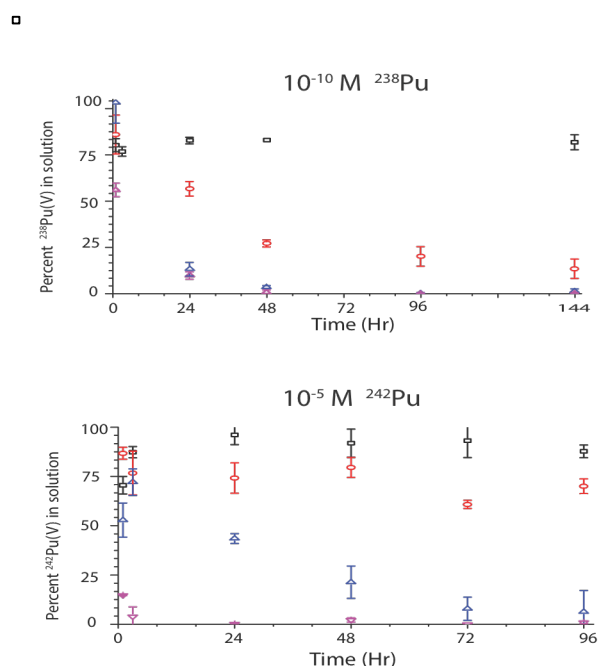

Figure E2. Kinetics of Pu(V) reduction by EPS. Black squares – No EPS. Red circles – 1 ppm EPS. Blue triangles – 10 ppm EPS. Magenta triangles – 25 ppm EPS.

In addition to characterizing the composition and functional groups of the EPS, we have also examined the Pu redox chemistry with bound-EPS (Fig. E2). We hypothesized that the bound-EPS could control the redox behavior of Pu. To test our hypothesis, the kinetics of Pu(V) reduction by EPS were investigated using bound-EPS isolated from strain *Pseudomonas sp* ESP-1. We investigated the reduction of Pu(V) to Pu(IV) in the presence of three different concentrations of EPS (25, 10 and 1 ppm) and two different Pu(V) concentrations. At Pu concentrations below solubility (~10^{-10}M), the Pu(V) was effectively reduced to Pu(IV) onto the EPS surface (>90%) at all three concentrations. The rate of reduction was fastest at the highest concentration of EPS and the slowest at the lowest concentration. At concentrations above solubility (~10^{-5} M), the Pu(V) was also effectively reduced at high concentrations of EPS but not at the lowest concentration (1 ppm) where we believe there was insufficient EPS to drive reduction.

In FY15, we will use NMR to further differentiate the functional groups within these macro-molecules and identify the groups that interact with Pu. We will compare NMR spectra of EPS before and after Pu binding. NMR is an ideal technique for heavy metal-EPS interactions as we can apply multiple NMR active nuclei (H^1, C^{13}, and P^{31}) to identify heterogeneous complexes (e.g., combinations of sugar, peptides, phosphates). We can also track peak shifts in spectra, due to the paramagnetic nature of Pu, in order to determine which functional groups and constituents are involved in complexation. By utilizing ^{13}C enriched EPS we will be able to acquire spectra at rates that allow us to probe the kinetics of Pu reduction with EPS.

Task E2: Investigate the Mechanisms of Pu-Microbe Interactions

This research effort was restarted upon restoration of funding in FY14.

In order to assess the role of microbes in the biogeochemical cycling of Pu, a series of Pu sorption experiments were carried out with *Pseudomonas sp.* strain EPS-1 isolated from NNSS at pH 6.8 with Pu(IV) and Pu(V). Plutonium concentrations were held at 10^{-10} M and the concentration of *Pseudomonas* cells varied between 10^8 and 10^6 cells/mL (Fig. E3). For comparison, two cell types were prepared, cells with bound-EPS and cells without their bound-EPS. In the experiment with Pu(IV) the Pu sorbed to both the EPS and the cell surfaces. At cell concentrations of 10^8 cell/mL, approximately 75% of the Pu(IV) attached to the surface of either the cells or the bound-EPS. In the Pu(V) experiments, significantly different behavior was observed. In the samples with the highest cell concentrations (10^8 cell/mL), over 80% of Pu sorbed to cells with bound-EPS while only 22% of Pu(V) sorbed to cells with the EPS removed. The lack of sorption of Pu(V) on cells without bound-EPS suggests that EPS drives the reduction of Pu(V) to Pu(IV). The oxidation state of Pu remaining in solution during both Pu(IV) and Pu(V) experiments was monitored by LaF$_3$ precipitation. Results indicate that in experiments where bound-EPS was present, the dominant oxidation state of Pu in solution was +4, independent of the initial oxidation state used. Conversely, in the case where the bound-EPS was removed, the oxidation state in the aqueous phase was not altered from that of the initial. This indicates that EPS can control the redox cycling of Pu, consistent with Pu reduction by purified EPS as described in Task E1.

To further examine the morphology, structure, and mineral phase of Pu sorbed to the cell surface, we used High-Resolution Transmission Electron Microscopy (HRTEM). For HRTEM sample preparation, we equilibrated EPS-bound strain ESP-1 with 1×10^{-4} M ^{242}Pu(IV) and ^{242}Pu(V) before the cells were fixed with formaldehyde, washed and dried on TEM copper grids for analysis. In the experiment starting with Pu(IV), the HRTEM analysis revealed large concentrations of PuO$_2$ colloidal precipitates (Figure E3-B). In contrast, when Pu(V) was equilibrated with cells no crystalline nano-colloids were observed, although the presence of monomeric Pu was detected on the cell by Energy Dispersive X-ray Spectroscopy (EDS). These data indicate that reduction of Pu(V) by bound-EPS does not generate Pu nano-colloids, even at concentrations well above Pu(IV) solubility.

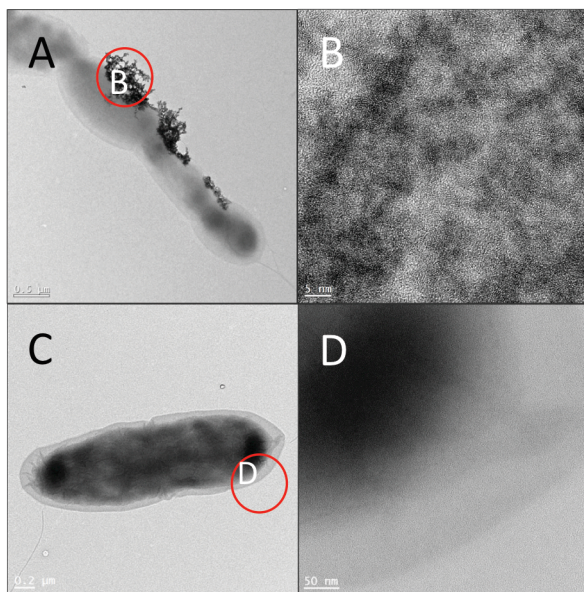In FY15 we will continue our experiments ranging from

Figure E3. Sorption of Pu(IV) (A.) and Pu(V) (B.) onto pseudomonas cells at pH 6.8 in the presence (filled symbols) and absence (open symbols) of bound EPS.

Figure E3. Pseudomonas equilibrated with 1×10^{-4} M ^{242}Pu at pH 6.5. **A.)** TEM image of Pu(IV) and cells. **B.)** HRTEM image of A showing crystalline Pu(IV) nano-colloids. **C.)** TEM image of Pu(V) and cells **D.)** HRTEM image of C showing only amorphous features.
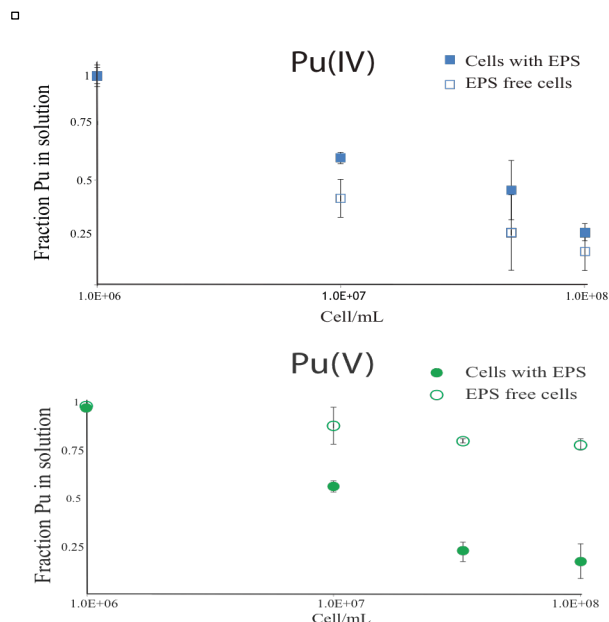
basic phase identification to high-resolution analytical studies to further define and characterize the EPS-facilitated Pu nano-precipitates on cell surface. Further analysis will also be carried out to determine if morphological surface structure is dependent on Pu concentration. By utilizing the high spatial resolution of energy dispersive spectroscopic techniques, e.g., TEM and NanoSIMS, we will be able to map Pu elemental distributions on the cellular level. These experiments will help define and characterize the Pu precipitates catalyzed by *Pseudomonas sp.* strain EPS-1, and provide important insights on the detection of a possible biogenic Pu mineral phase as a way to assess the microbial contribution to Pu transport chemistry and immobilization.

Task E3: Integrated Program Experiments: Biofilm-Pu Interaction in the Presence of Minerals (*Contingent upon increase in budget*)

The microbial Program Element E has been designed to integrate with and inform Program Elements A, B, and D. We aim to achieve full characterization of the Pu behavior in a biofilm system with respect to 1) the spatial organization of cells and EPS within the biofilm, 2) the nature Pu absorption, and Pu partitioning between EPS and microbes during biofilm development, and the overall absorption capability of biofilm (Figure E2). We are particularly interested in identifying different environmental factors that cause these system properties to change and to develop a set of methods to quantify that change. To perform these biofilm experiments, we will first genetically label fluorescent markers on *Pseudomonas* in order to facilitate downstream microscopic characterization. Our first goal is to determine how *Pseudomonas* colonize glass surfaces and form a community. We will compare biofilm formation on mica surfaces to biofilm formation on glass and how Pu behavior changes on different functional surfaces. The effect of colloidal montmorillonite will also be tested in the biofilm

experiments (Figure E2, right panel). Biofilm development (days to weeks) will be performed on an inverted fluorescent microscopy in our laboratory. A flow cell that is routinely employed in biofilm labs for microscopic imaging will be used to perform these experiments (Whiteley *et al.*, 2001). The advantage of the flow cell is that it permits the spatial tracking of individual cell from early to late time points in the development of a biofilm. The composition and flow rate of the medium passing through the chamber (including Pu) can also be precisely controlled. Biofilm at different time points will be harvested. We will determine cell mass and composition of the EPS.

Figure E2. Diagram illustrating Pu adsorption to reactive surfaces in biofilms in the absence (left) and presence (right) of clay minerals. Orange colored cells can be either planktonic or biofilm state, which is embedded in the EPS matrix (green). Clay minerals (chocolate colored pentagons) can absorb Pu directly or mediated by cell or EPS surfaces.

After we have characterized Pseudomonas biofilm formation, we will characterize the Pu adsorption behavior on biofilm. We will experiment with adding low concentrations of Pu at the beginning of biofilm formation, as well as adding more concentrated Pu to a pre-formed biofilm. Microscopic characterization of Pu absorption onto biofilm will be performed as described in Task E2. Questions of interest to us include: How much and under what conditions will Pu sorb to the biofilm? Over what time scales will this absorption occur? Is Pu absorption a function of EPS concentration? When will the Pu absorption reach a static state within the biofilm?
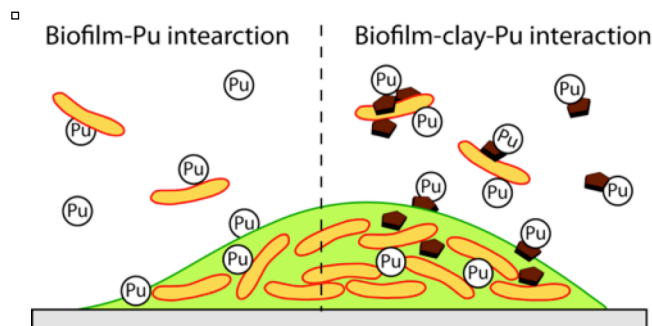
4.a.ii Scientific Highlights

Pu(IV) has a similar affinity for mineral surfaces over a ten orders of magnitude range of Pu concentrations (10^{-7} to 10^{-16} M). Importantly, our experimental data accumulated in the past four years indicates that the affinity of Pu for mineral surfaces will not increase significantly at ultralow Pu concentrations (10^{-16} M) compared to higher concentrations routinely used in the laboratory (10^{-9} M). These results are reassuring in that processes identified at moderately high concentrations ($<10^{-9}$ M) can be scaled to processes at ultra-low environmental concentrations. These results have broad implications to our conceptual understanding of processes controlling colloid facilitated Pu transport and, more broadly, to contaminant reactive transport (Begg *et al.*, 2014).

Pu(IV) has a similar affinity for bentonite over a ten orders of magnitude range of Pu concentrations (10^{-7} to 10^{-16} M). Pu(IV) and Pu(V) sorption to bentonite was broadly linear at initial Pu concentrations ranging from 10^{-7} mol/L to 10^{-16} mol/L. These results indicate that Pu adsorption by bentonite is likely controlled by the montmorillonite component of the clay (92%) and that the other minor mineral phases do not significantly alter the Pu adsorption process.

Development of a consistent model for Pu adsorption/desorption interactions with montmorillonite. A mechanistic model was developed that can reproduce adsorption and desorption data for Pu(IV) interactions with montmorillonite at pH 6 and pH 8. As a result we are able to identify mechanisms for future study as well as make testable predictions about the mobility of Pu in the environment.

Demonstrated a H_2O_2 - driven desorption of Pu(IV) from mineral surfaces. We have performed experiments demonstrating the ability of a commonly occurring chemical to effect the desorption of Pu from mineral surfaces at environmentally realistic concentrations. This result has implications both for our understanding of the mechanisms of Pu desorption as well as the stability of Pu adsorbed on mineral surfaces (Begg *et al.,* 2014).

Ab initio MD simulations are an invaluable tool for probing atomic-scale dynamics. Our work represents an important test for the validity for the alumina/water interface, a case where high-quality experimental data are available for comparison. The simulations have also enabled us to provide a molecular explanation for the "ice-like" and "liquid-like" bands observed in sum-frequency vibrational spectroscopy experiments, whose interpretation was previously unclear and speculative (Huang *et al.*, 2014).

Cation composition of water (Na^+, K^+, Mg^{2+} and Ca^{2+}) affects the adsorption of neptunium on clay by ion exchange. We determined a Np(V)-montmorillonite ion exchange constant that is applicable across a wide range of ionic strength and solution cation compositions. We developed a model for Np(V) ion exchange consistent with

accepted major cation exchange coefficients reported in the literature that can be readily applied in thermodynamic databases. Identified solution conditions at which Np(V) ion exchange will play a significant role in retarding Np(V) migration in the environment (Benedicto *et al.,* 2014).

The presence of NOM in goethite suspensions decreased the fraction of Pu associated with the goethite by stabilizing Pu through the formation of soluble Pu-NOM complexes. The degree of Pu solubilization by NOM (DFOB> fulvic acid > humic acid > citric acid) reflects the strength and stability of the Pu-NOM complexes. Modeling the observed data indicates sorption is influenced by formation of ternary surface-NOM-Pu complexes at low pH.

Using Fourier Transform Infrared Spectroscopy (FTIR-ATR) we have confirmed the specific nature of NOM binding to goethite. These observations help to explain enhanced sorption observed in ternary Pu-NOM-mineral systems at low pH due to the potential formation of a mineral-NOM-Pu ternary surface complex.

Batch and flow-through experiments examining Pu sorption/desorption to goethite in the presence of NOM indicate that an aging process occurs in which the strength of the Pu-surface complex increases with time. This is manifested by decreased rates and extent of Pu desorption from goethite with increasing equilibration times.

The strong affinity of aqueous Pu(IV) for the goethite surface is explained by the epitaxial growth of bcc Pu_4O_7 nano-particles on goethite. The surface precipitation of 3-5 nm Pu_4O_7 nano-particles appear to be stable over the timescale of months at both 25 and 80°C. There is no indication that the Pu_4O_7 alters to PuO_2 over time (Zavarin *et al.,* 2014).

Alteration and characterization of nuclear melt glass shows that the original melt glass altered to secondary clay and zeolite colloids. Pu activities in solution are less than 1 nCi/L in all cases. Pu desorption experiments recently initiated that Pu desorption of the melt glass is much less reversible than simple surface desorption processes.

Np(VI)-carbonate exchange rates was experimentally determined using NMR to be 40.6 s^{-1} for the triscarbonato complex at a pH higher than nine. The Np(VI)-carbonate exchange rates were determined to be pH-dependent below pH 9 (Panashi *et al.* 2014). The saturation transfer technique shows great promise to elucidating the fundamental reaction rates of the actinides.

Examination of Pu redox chemistry in the presence of bound-EPS and the microbe, Pseudomonas sp, show that EPS will control the sorption behavior of Pu. Pu(V) was reduced to Pu(IV) by EPS. TEM results suggest that Pu associated with bound EPS at the cell surface is amorphous.

4.a.iii Summary of Publications

1. Begg, J.D., Zavarin, M., and Kersting, A.B., (2014) Plutonium desorption from mineral surfaces at environmental concentrations of hydrogen peroxide. Env. Sci. & Tech. 48 (11), 6201–6210 DOI: 10.1021/es500984w

2. Zhao, P., Tinnacher, R. M., Zavarin, M., and Kersting, A. B. (2014). Neptunium Transport Behavior in the Vicinity of Underground Nuclear Tests at the Nevada National Security Site. *In press* . J. Environmental Radioactivity

3. Benedicto, A., Begg, J.D., Zhao, P., Kersting, A.B., Missana, T., and Zavarin, M. (2014) Effect of major cation water composition on the ion exchange of Np(V) on montmorillonite: NpO^{2+}-Na^+-K^+-Ca^{2+}-Mg^{2+} selectivity coefficients. *Applied Geochemistry*. DOI: 10.1016/j.apgeochem.2014.06.003.

4. Zavarin, M., Zhao, P., Dai, Z.R., and Kersting, A.B. (2014) Plutonium Sorption and Precipitation in the Presence of Goethite at 25 and 80°C *Radiochimica Acta*. DOI 10.1515/ract-2013-2188.

5. Parson-Moss, T., Wang, J., Jones, S., May, E. Olive, D., Dai, Z., Zavarin, M., Kersting, A.B., Zhao, D., and Nitsche, H. (2014) Sorption Interactions of Plutonium and Europium with Ordered Mesoporous Carbon. DOI: 10.1039/c4ta01740d.

6. Boggs, M.A., Mason**,** H.E., Arai, Y., Powell,.A., Kersting, A.B., Zavarin, M. (2014) Determination of Plutonium (IV) Desferroxamine B structures in aqueous solution by nuclear magnetic resonance spectroscopy, *European Journal of Inorganic Chemistry*. DOI: 10.1002/ejic.201402105.

7. Panasci, A.F., Harley, S.J., Zavarin, M., Casey, W.H. (2014) Kinetic Studies of the [NpO2(CO3)3]4-Ion at alkaline conditions using 13C NMR. *Inorganic Chemistry* 53, 4202-4208.

8. Huang, P., Pham, T.A., Galli, G. and Schwegler, E (2014) Alumina(0001)/Water interface: Structural properties and infrared spectra from first-principles molecular dynamics simulations. *J. Physical Chemistry.* http://dx.doi.org/10.1021/jp4123002

9. Zimmerman, T., Zavarin, M., Powell, B. A., (2014) Influence of humic acid on plutonium sorption to gibbsite: Determination of Pu-humic acid complexation constants and ternary sorption studies. *Radiochimica Acta*, DOI 10.1515/ract-2014-2163.

4.b   FUTURE SCIENTIFIC GOALS

Program Element A:
- Complete flow cell desorption experiments to quantify rates of Pu desorption from goethite and montmorillonite. Develop a comprehensive model for Pu sorption/desorption with these minerals and begin assessing the implications of desorption kinetics on actinide transport in the environment.
- Develop ab-initio model of the hematite(0001)/water interface and initiate simulation of Pu adsorption to that surface. Extend our study of the relationship between axial hydroxide ligands of Pu(IV) and axial –yl oxygen ligands of Pu(V) and the implications to redox processes.

Program Element B:
- We will use ligand competition/ultrafiltration experiments with polymerized aspartic acid (PAA) and desferrioxamine B (DFOB) to determine the stability constants of Pu-FA complexes across the pH range 3-9. These stability constants will then be used to predict Pu speciation in batch sorption and reactive transport models.
- We will expand our studies of ternary complex formation by examining the role of organic compounds in the subsurface transport of Pu in soils and sediments.

Program Element C:
- We will investigate samples from another contaminated field site (e.g. LANL, NNSS) and characterize the occurrence and location of Pu using NanoSIMS and TEM. The results will be compared to our study at Hanford and this information will allow us to understand how Pu is transported in diverse geologic settings and to what extent colloids play a role in Pu transport.
- We will be use state-of-the art TEM capability to test the hypothesis that the structure of the precipitate is a function of its molecular-scale relationship at the mineral-water interface and evaluate these implications for long-term Pu transport. In particular, we will examine the nature and morphology of Pu surface precipitates on structural and non-structural analog of goethite.

Program Element D:
- We will complete our characterization the secondary mineralogy produced as a result of glass alteration. A series of Pu desorption experiments on altered material will be performed and compared to flow cell desorption experiments performed in Program Element A. These experiments are critical to identifying the stability of Pu associated with colloidal glass alteration products and determine if actinides are able to coprecipitate into these secondary phases.
- We plan to explore interactions between Pu and mineral surfaces using the NMR techniques we have developed in this program. Of particular importance will be the investigation of polymer and surface precipitate formation that can affect the stability of Pu on mineral surfaces and, as a consequence, the effectiveness of colloid-facilitated transport. The effort will be expanded by taking advantage of sample spinning capabilities available at EMSL.

Program Element E:
- We will use NMR to identify the functional groups involved in Pu(V) reduction and sorption on EPS. NMR will also be used to characterize functional group variability among a set of microbial isolates to study variations in Pu sorptive and reductive capacity among microbes.
- If funding is available, we plan to expand our study of biofilm and EPS interaction with Pu with respect to 1) the spatial organization of cells and EPS within the biofilm, 2) the nature Pu absorption, and Pu partitioning between EPS and microbes during biofilm development, and the overall absorption capacity under dynamic biofilm growth.

4.c   NEW SCIENTIFIC RESULTS—*SEE SECTION 4.a.ii*

4.d   COLLABORATIVE RESEARCH ACTIVITIES

We have a sub-contract to collaborate with Brian Powell at Clemson University, SC to work on Program Element B. Details of the work are discussed in section 4.a.i, Program Element B. We have one unfunded research collaboration with Andy Felmy (PNNL) to investigate contaminated samples from Hanford. Details and results from these collaborations can be found in Section 4.a.i, Program Element C, Task C2.We have 7 students working at LLNL over this past year. Chad Durant from U. Pennsylvania, Jennifer Logan from UC Irvine, Tashi Parson-Moss, Eva Uribe, and Jennifer Shusterman from UC Berkeley, Ana Benedicto from CIEMAT, Spain, and Jewel Wrighton from S. Carolina State University.

5.   STAFFING AND BUDGET SUMMARY

5.a   FUNDING ALLOCATION BY PROGRAM ELEMENT

5.a.i   Present Funding

In FY14 our SFA budget was 1.0M

Program Element	Costs ($K)		LLNL Researcher	Effort	Cost ($K)
Program Element A	280		Annie Kersting	10%	50
Program Element B *(+Subcontract Clemson Univ.)*	320		Mavrik Zavarin	50%	250
Program Element C	80		Pihong Zhao	5%	40
Program Element D	120		Zurong Dai	5%	40
Program Element E	200		Yongqin Jiao	10%	30
			Ben Jacobsen	20%	60
			Mark Boggs	100%	150
			James Begg	100%	200
			Harris Mason	20%	80
			Claudia Joseph	50%	80
Total	**1.0M**		Scott Tumey	10%	50

5.b   FUNDING FOR EXTERNAL COLLABORATORS

We have an external collaboration with Brian Powell at Clemson University, SC for Program Element B: Stabilization of Pu Surface Complexes on Mineral Colloids by NOM. We expect this collaboration to our SFA and will continue at approximately $110K/yr.

5.c   PERSONNEL ACTIONS

We hired a postdoc in August FY13 and converted a postdoc to a staff position in January 2014.

5.d   NATIONAL LABORATORY INVESTMENTS

The Seaborg Institute covers all of the administrative costs to execute this program, and approximately 10% of an administrator's time. In addition, the SEM operational cost is also covered under the Institute's operating budget. Annie Kersting, Director of the Seaborg Institute oversees a summer student program that paid for the cost of three summer students working on this program in FY13. As an institution, LLNL subsidizes the cost of all postdocs by 25%.

5.e   CAPITAL EQUIPMENT

Several pieces of equipment were purchased in FY13 via cost sharing with other programs that will directly benefit BER. They include a low-level organic carbon analyzer (Shimadzu), Metrohm anion/cation chromatograph, and others. In addition, LLNL

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